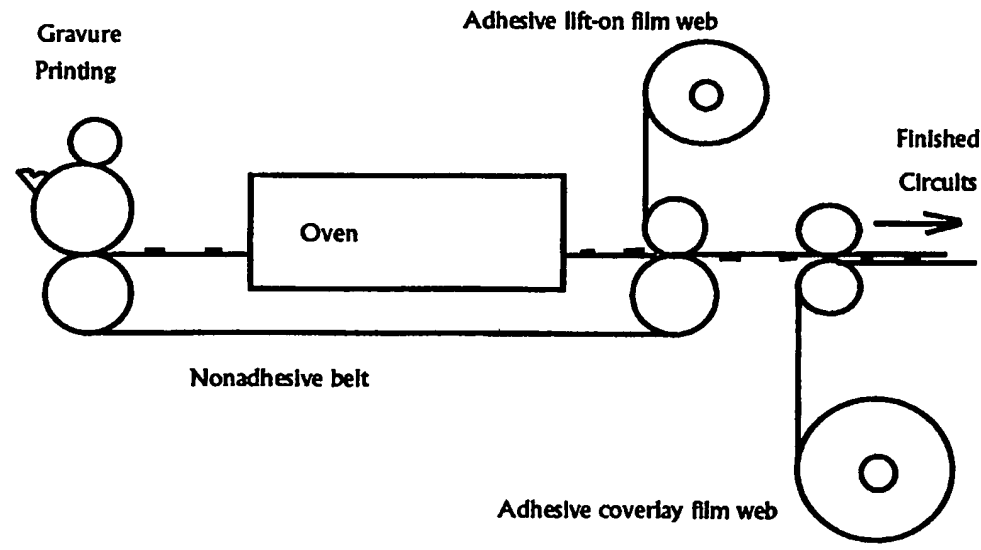


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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US98/20420 <b>(22) International Filing Date:</b> 30 September 1998 (30.09.98) <b>(30) Priority Data:</b> 60/060,522 30 September 1997 (30.09.97) US <b>(71) Applicant (for all designated States except US):</b> PARTNER-SHIPS LIMITED, INC. [US/US]; 32 Woodlane Road, P.O. Box 6042, Lawrenceville, NJ 08648 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> KYDD, Paul, H. [US/US]; Partnerships Limited, Inc., 32 Woodlane Road, P.O. Box 6042, Lawrenceville, NJ 08648 (US). <b>(74) Agents:</b> NISSIM, Stuart, H. et al.; Woodbridge & Associates, P.C., P.O. Box 592, Princeton, NJ 08542-0592 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> MANUFACTURE OF THIN METAL OBJECTS   <b>(57) Abstract</b> <p>A process is disclosed whereby paste and ink PARMOD™ compositions printed on a thermally stable material and cured in an oven to create metal foil objects such as electronic circuits, instruments and decorations. The metal foil objects can be lifted onto adhesive substrates to produce electronic circuit boards and similar products.</p>		

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## **Manufacture of Thin Metal Objects**

### **Background of the Invention**

In the microelectronics industry the basic method for forming circuit traces on a substrate involves a combination of photoresist and electroplating steps which incorporate many hazardous and expensive compounds and solvents and involves extensive processing of the circuit board/substrate. One attempt to avoid the repeated processing of the substrate involves forming the circuit traces on a metallic board using the photoresist/electroplating processes or by die cutting the circuit patterns from a metal foil. An adhesive is then used to transfer the circuit to the substrate.

Another alternative is the "lift off" method. In this process an adhesive image of the circuit traces is formed on the substrate. A metal foil is then bonded to the adhesive image and the unwanted foil not bound to the adhesive image is then lifted off by an adhesive film.

These methods can be used, for example, when the substrate can not endure the circuit forming processes. However, the extensive processing and substantial expense are prohibitive to commercialization and mass production.

### **Brief Summary of The Invention**

A novel family of compounds, commercially available as PARMOD™ compositions from Parelec, LLC, which are disclosed in Applicants' co-pending PCT Application PCT/US97/16226 filed 12 September 1997, the application in total being hereby incorporated by reference. These compositions can be formulated into printing inks or pastes. These inks can be printed on a substrate and cured to well-consolidated films of pure metal in seconds. The fast curing capability of PARMOD™ compositions, as well as their ready application, makes it possible to use them to create complex thin

metal objects by very simple and low-cost processes. An example of such an object is a pattern of electrical conductors used as an antenna in a radio frequency identification tag. Another such application is as a TAB bonding decal for semiconductors. Electronic circuit patterns of many types can be produced by this process and bonded to various types of substrates and devices. the method can be used to produce strain gauges, thermocouples and other types of instrumentation. Many other such objects and applications will be evident to those skilled in the art.

The PARMOD™ compositions can be printed directly on a substrate to be used in the final product, and it would therefore be important to obtain a good bond to the substrate. Furthermore, the substrate would have to withstand the temperatures at which the PARMOD™ compositions cure to solid metal. These requirements impose severe restraints on the substrate materials which have to have a surface or a coating to which PARMOD™ will bond and have to have high temperature capability. Both requirements tend to limit the selection and increase the price of the substrate. This is particularly difficult in that the low cost copper PARMOD™ mixture requires the highest cure temperature and is limited to expensive polyimide substrates.

The present invention decouples the curing and adhesion processes from the substrate by doing the printing and curing on a temporary substrate and then transferring the metal foil object produced to a permanent substrate at low temperature. Desired characteristics of the temporary substrate are: that the PARMOD™ not permanently bond to it; that it have approximately the same coefficient of thermal expansion as the PARMOD™; that it withstand the temperature at which the PARMOD™ cures; and, that it be easily reusable or very inexpensive.

The preferred PARMOD™ compounds contain a Reactive Organic Medium (ROM) and a source of metal, preferably metal flakes, metal powders and their mixtures. The ROM consists of either a Metallo-Organic Decomposition (MOD) compound or an organic reagent which can form such a compound upon heating in the presence of the metal source. The ingredients are blended together with rheology modifying organic vehicles well known in the art, if necessary, to produce printing inks or pastes. These inks can be printed on a substrate and cured to well-consolidated films, traces and objects of pure metal in seconds.

The process can be performed continuously, for example, using belts and tapes or webs. Likewise, using a series of belts, tapes and webs, multilayered units can be produced

#### **Brief Description of the Drawings**

Preferred embodiments according to the present invention will be described in detail with reference to the following figures, wherein:

Figure 1. is an illustration of a continuous process using the method of the invention to form substrates having metal circuit traces, components, and objects.

Figure 2 is an illustration of a continuous process using the method of the current invention to form multilayered circuits.

Figure 3. Is an illustration of a tape automated bonding decal formed using the current method.

#### **Detailed Description of the Invention**

Preferred compositions useful for forming the traces, components and objects are comprised of a metal mixture and a Reactive Organic Medium (ROM). These compositions can be applied to thermally stable substrates and cured to well-consolidated circuit traces and objects by heat treatment. The compositions exhibit a critical temperature above which they undergo a transformation to well-consolidated electrical conductors with a resistivity only two to four times the bulk resistivity of the metal in question. The electrical conductivity is equal to that obtained by conventional high temperature metal powder sintering in conventional thick film compositions on ceramic substrates. Remarkably, this consolidation process takes place at temperatures 400 to 500 degrees Celsius lower than with compounds conventionally used in thick film technology, and in times which are an order of magnitude shorter than are required for sintering.

Suitable metals include copper, silver, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, cobalt, nickel, indium, tin, antimony, lead, bismuth and mixtures thereof. Examples of typical proportions of PARMOD™ mixtures containing an organic acid as the ROM and both metal flakes and colloidal metal powder are illustrated in Table 1 as follows:

**TABLE 1**                      **Acid-Based PARMOD™**

	Metal Flake	Metal Powder	Organic acid	Organic vehicle
Range	20-60%	10-45%	5-35%	0-35%
Preferred	40-60%	24-44%	5-20%	0-10%
Most preferred	40-60%	24-44%	10-20%	0-5%

Percents by total weight of the composition.

In a preferred embodiment, the metal mixture contains metal flake and colloidal or semi-colloidal metal powder where the total of flake plus powder is preferred to be 60-85% of the total mixture, and the powder is preferred to be 30-50% of the total metal. Larger amounts of organic vehicle may be added to reduce viscosity for certain applications.

The metal flakes have a major dimension between 2 to 10 micrometers, preferably about 5 micrometers, and a thickness of less than 1 micrometer. They can be produced by techniques well known in the art by milling the corresponding metal powder with a lubricant, which is frequently a fatty acid or fatty acid soap. The starting powders are usually produced by chemical precipitation to obtain the desired particle size and degree of purity. The flakes are sold for electronic applications as constituents of thick film inks and silver-loaded conductive epoxies.

The flakes perform several functions. They form a skeleton structure in the printed image which holds the other ingredients together and prevents loss of resolution when the mixture is heated to cure it. The flakes naturally assume a lamellar

structure like a stone wall which provides electrical conductivity in the direction parallel to the surface of the substrate and provides a framework to lessen the amount of metal transport necessary to achieve the well-consolidated pure metal conductors which are the objective of this invention. They also provide low surface energy, flat surfaces to which the other constituents of the composition can bond.

The other metallic powder mixture constituent of the present invention are preferably colloidal or semi-colloidal powders with individual particle diameters below about 100 nanometers, preferably less than about 50 nanometers. The colloidal or semi-colloidal powder is preferably present in about 40% by weight of the total weight of the metal powder mixture. A primary function of these powders is to lower the temperature at which the compositions will consolidate to nearly solid pure metal conductors. The presence of fine metal powder has been found to be helpful in advancing this low temperature process with silver and essential to the consolidation of copper mixtures. It is important that they be present as individual particles. Metal particles this small have a strong tendency to agglomerate into aggregates with an open skeletal structure.

Colloidal silver particles with a nominal diameter of 20 nanometers were shown to have an excellent state of dispersion and have been used in silver compositions and lowered the critical consolidation temperature from 300 to 260 degrees C.

To achieve and preserve the desired degree of dispersion of colloidal metal it is essential to stabilize the particles so that they cannot aggregate. In the case of the silver particles they were stabilized by the presence of a surfactant which coated the surface of the particles and prevented metal-to-metal contact. Suitable surfactants include carboxylic acids and metal soaps of carboxylic acids. This favors chemical precipitation as a means of producing the powders, since they can be exposed to an environment which promotes stabilization from formation to final consolidation.

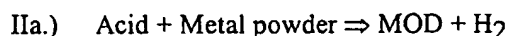
The Reactive Organic Medium (ROM) provides the environment in which the metal mixture is bonded together to form well-consolidated conductors. Many classes of organic compounds can function as the ROM. The common characteristic which

they share and which renders them effective is that they have, or can form, a bond to the metal via a hetero-atom. The hetero-atoms can be oxygen, nitrogen, sulfur, phosphorous, arsenic, selenium and other nonmetallic elements, preferably oxygen, nitrogen or sulfur. This bond is weaker than the bonds holding the organic moiety together, and can be thermally broken to deposit the metal. In most cases the reaction is reversible, so that the acid or other organic residue can react with metal to reform the metallo-organic compound, as shown schematically below:

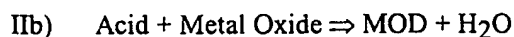


where R is a reactive organic compound and M is the metal.

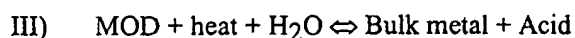
As an illustration of PARMOD™ mixtures containing MOD forming constituents such as organic acids, the reactions which take place in curing are as follows:



or



and

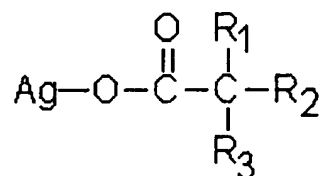


The effect is to consume the small particles and weld together the big ones to create macroscopic circuit conductors of pure metal. In place of acid, some other active organic reagent which will produce an easily decomposed metallo-organic compound from either the oxide or the metal could be used. An example would be the use of sulfur compounds to make mercaptides or nitrogen ligands to produce decomposable complexes.

Examples of useful compounds are soaps of carboxylic acids, in which the hetero-atom is oxygen; amino compounds, in which the hetero-atom is nitrogen; and mercapto compounds, in which the hetero-atom is sulfur.

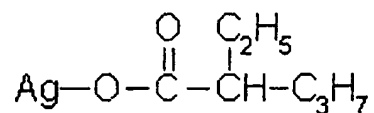


Specific examples of preferred ROM constituents are the carboxylic acids and the corresponding metallic soaps of neodecanoic acid and 2-ethyl hexanoic acid with silver and copper, such as. silver neodecanoate illustrated by the formula:

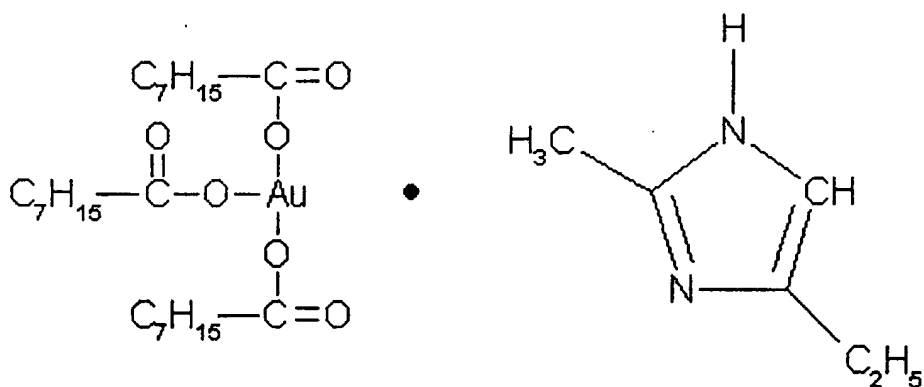


where  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  are  $\text{C}_9\text{H}_{19}$

and silver 2-ethyl hexanoate as illustrated by the formula:

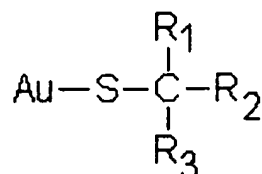


Gold amine 2-ethyl hexanoate is an example of a nitrogen compound.:



*Gold amine 2-ethyl hexanoate (gold amine octoate)*

Gold t-dodecyl mercaptide is an example of a sulfur compound:



where  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  are  $\text{C}_{11}\text{H}_{23}$

These ROM compositions can be made by methods well known in the art. All of the above compounds are capable of decomposition to the respective metals at relatively low temperatures. For the silver neodecanoate and silver 2-ethyl hexanoate (silver octoate), the decomposition temperature is between 200 and 250°C. For the corresponding copper compounds, it is between 300 and 315 C. Gold sulfides decompose at very low temperatures in the neighborhood of 150°C. Gold amine octoate decomposes between 300 and 500°C. The copper and silver compounds can be reformed from the corresponding acids at the same temperature, so the reaction is reversible, as mentioned above.

In some cases it is convenient to add rheology-enhancing compounds well known in the art to improve the printing characteristics of the compositions of the invention. Alpha-terpineol has been used to reduce the viscosity of copper and silver compositions to facilitate screen printing. Alpha-terpineol also participates in the consolidation reaction by virtue of the acid character of the OH group bonded to an unsaturated ring. By selecting constituents and additives, it has proven possible to produce a range of printable compositions ranging from fluid inks with a viscosity of 15 centipoise to solid powders.

The composition is printed on the substrate using any convenient printing technology. Screen printing and stenciling are suitable for rigid substrates in relatively small numbers with high resolution. Gravure printing, impression printing and offset printing are suitable for high production rates on flexible substrates. Ink jet printing and electrostatic printing offer the additional advantage of direct computer control of the printed image. This permits circuits to be printed directly from Computer Aided

Design (CAD) files and eliminates the need for special tooling. Each circuit can be different, if desired, for coding or prototyping. The same end can be achieved at lower production rates with computer- controlled dispensing equipment. This equipment produces dots or lines by moving a needle over the surface and dispensing printing composition supplied by a pump or pressurized syringe.

Compositions of this invention have been applied by screen printing, stenciling, dispensing, gravure printing, ink jet printing, impression printing, offset printing and electrostatic printing. Alternative application methods include coating an adhesive pattern with a dry powder composition or toner. Screening, as used in applying conventional thick film pastes has been used most extensively for preparing samples for evaluation. A composition with a viscosity of approximately 500 poise is forced through a fine screen with a photo-defined open image of the desired conductor pattern in it by a rubber squeegee. The resolution which has been achieved by this method is approximately 125 micron (5 mil) lines and spaces, although production screen printers can achieve patterns as fine as 50 microns. Conductive traces with thicknesses up to 50 microns have been printed, though most of the test patterns have been in the neighborhood of 12 microns thick, which is equivalent to 0.37 ounces of copper per square foot.

When the metallo-organic decomposition compound or the acid from which it is formed is mixed with the metal flake and colloidal metal powder constituents described above, printed as a relatively thin layer on an appropriate substrate, and heated to a critical temperature above the decomposition temperature of the metallo-organic compound, a reaction takes place which results in the sudden consolidation of the loosely aggregated metal constituents into a nearly solid metal trace with greatly reduced electrical resistivity. Scanning Electron Micrograph cross sections of traces which have been heated to decompose the metallo-organic compound but below the critical temperature for copper and for silver mixtures show the individual metal flakes and powder particles, much like a picture of the unheated mixture.

When the traces are heated above the critical temperature, there is a very rapid decrease in electrical resistivity, a dramatic increase in mechanical cohesive strength of

the deposit and the appearance of the deposits changes. SEM cross sections of copper, silver and gold mixtures that have been heated above the critical temperature show that the metal flake and powder have consolidated into a bonded network of solid metal.

The compositions are cured by exposure to heat for a short period of time. This time varies with the temperature to which the substrate can safely be exposed, but is less than a minute to achieve most of the electrical conductivity of which the composition is capable, and in some cases is less than 10 seconds at temperature.

For copper (and gold) the critical temperature is in excess of 300°C . Between 305 and 325°C the resistivity of copper traces dropped by a factor of 100 to a value below 10 microohm-cm. The bulk resistivity of copper is 1.7 microohm-cm. At the same temperature at which the resistivity drops the mechanical properties of the traces improved equally dramatically. From being brittle and poorly adherent as measured by creasing the samples and pulling the traces off with Scotch Tape the samples become ductile enough to survive a sharp 180 degree crease in the 75 micron (3 mil) substrate followed by tape testing. The crease test is equivalent to an elongation of the metal trace of 17%. The tape test is equivalent to an adhesion of approximately 10 Newtons/cm (6 lb per lineal inch) Heating to still higher temperatures decreases the resistivity only slightly.

For silver, the decrease in resistivity with processing temperature is not as dramatic as with copper but the conversion from a poorly-consolidated material which is easily fragmented to a ductile metal is equally sharp. The critical temperature is approximately 230°C .

The critical temperature can be adjusted by mixing metallo-organic constituents. As mentioned above, gold amine octoate decomposes at temperatures up to 500°C . This is too high for use with polymer-based printed circuit substrates or most other electronic components. Gold t-dodecyl mercaptide decomposes at approximately 150°C . This is too low to bond effectively with the substrates of interest or with added gold flake. Gold neodecanoate decomposes at about 120-154°C. A mixture of gold amine octoate and gold neodecanoate has been used to achieve a decomposition temperature in the desirable range.

Both gold and silver mixtures can be heated in air since the elemental metals are the stable form at the temperature at which the metallo-organic constituent decomposes. Copper, however, requires the use of a protective atmosphere to prevent the formation of copper oxide which is the stable product of decomposition in air. A nitrogen atmosphere containing less than about 20 and most preferably less than 3 ppm by volume of oxygen has been found to be suitable. Addition of water vapor in the amount of about 5% has proven to be helpful in improving the conductivity of the resulting deposits.

While the PARMOD™ should not bond to the thermally stable substrate, a certain amount of tackiness or adhesion may be desired when using an automated, continuous process. Substrates well known in the art will possess the characteristics required for the temporary substrate. Examples of suitable temporary substrates include, but are not limited to, polyimide films, polysulfone films, polyester films, teflon coated films, silicone coated films, metal foils, glass and ceramic surfaces.

The permanent substrate need only have the ability to bond reliably to the transferred metal foil in addition to any other requirements of the final application such as dielectric strength. Examples of suitable substrates include, for example, polyethylene, polypropylene, polystyrene, polyester, polycarbonate, polyurethane, cellulose and paper. Coatings of pressure sensitive or other types of adhesive known in the art may be used to accomplish this, for example, thermoplastic materials such as polyethylene or epoxy, phenolic, acrylic and polyimide thermosetting resins. It may also be accomplished by the thermoplastic or adhesive nature of the substrate itself, for example, polyethylene, polypropylene or polystyrene.

For still greater economies and higher production rates, the conductor pattern can be applied to a continuous web of substrate by a rotary press, much like printing a newspaper but with finer resolution, as shown in Figure 1. Gravure printing can be used in this application. Offset printing can produce very high resolution also. Ink jet printing and electrostatic printing at high speeds are candidates. Following the printing step, the circuits will be cured in an oven, still as a continuous web. The ability of these mixtures to cure to solid metal in seconds is critical to realizing this concept.

Longer processing times would make the oven disproportionately large relative to the press and squander much of the speed advantage of high speed printing. In a continuous process the PARMOD™ compound is printed in the desired patterns onto a belt of the thermally stable substrate. The belt passes through an oven in which the PARMOD™ is cured and forms solid metal objects. An adhesive face of a continuous "tape" of the permanent substrate is contacted with the belt and the metal objects are "lifted" onto the permanent substrate tape. The tape can then be laminated and cut to form individual circuit boards.

Multiple layers can readily be produced by this technology by using a double sided coverlay which will lift off another set of images as illustrated in Figure 2. A double sided dielectric is used to cover one layer and lift the metal objects onto the next layer. This double-sided dielectric can be, for example, a conventional prepreg consisting of glass cloth reinforcement impregnated with B-stage epoxy resin. The process may be continued for as many layers as desired to make multilayer circuit boards by a continuous, low-cost process.

Long term, for very high production runs, the newspaper analogy can be pushed further with multiple rotary presses turning out multiple metal objects simultaneously which are cured in a single oven and perhaps joined and laminated on the fly before die cutting to size. The stacks would be cut apart to create individual the circuits. A still less expensive approach is to use the adhesive on the back surface of single sided inner layers to laminate the stack without the use of prepreg.

The lift-on process can also be used to make partially supported patterned metal foil objects such as Tape Automated Bonding Decals. The pattern is printed on a nonadhesive material and lifted onto a die cut adhesive tape leaving part of the pattern exposed. The result is a tape with fine metal fingers which can be gang bonded to the pads on semiconductor chips. The outer ends of the fingers which are supported by the tape can be soldered to a semiconductor package or direct to a printed circuit for chip-on-board mounting. Such a TAB decal is shown schematically in Figure 3.

Other supported, partially supported and unsupported objects can be made by the technology of the present invention as can be appreciated by those skilled in the relevant arts. examples are:

Instrumentation such as thermocouples and strain gauges

Resistors, capacitors and inductors printed on polymer films

Electric heaters

Circuitry comprising any or all of the above, such as radio frequency tags which can be interrogated remotely for identification of packages and baggage

Decorative metallic items such as jewelry and Christmas ornaments

#### **Examples**

The examples described below indicate how the individual constituents of the preferred compositions and the conditions for applying them function to provide the desired result. The examples will serve to further typify the nature of this invention, but should not be construed as a limitation in the scope thereof. which scope is defined solely in the appended claims.

#### **Example 1**

A silver PARMOD™ screen ink was prepared as follows. 12.0 grams of Degussa silver flake, 3.0 grams of silver neodecanoate, and 1.35 grams of neodecanoic acid were mixed together using a spatula. The resulting mixture was then milled on a roll mill to give a homogeneous paste.

Images of an eight turn antenna coil and a capacitive plate were screen printed on separate substrates using silver PARMOD screen . The screen parameters were a 195 mesh screen backed with a 0.7 mil emulsion. The substrates used were 1 mil thick sheets of Kaladex® 2030 polyethylene naphthalate (PEN). The samples were thermally cured by heating to 210°C in a box furnace with an air atmosphere for

2-5 minutes. The resulting samples were continuous pure silver films with an electrical resistivity of  $3.5 \mu\Omega\text{-cm}$  and poor adhesion to the substrate.

The silver films were then transfer laminated to opposite sides of a 1.3 mil thick polyethylene (PE) substrate. The PE substrate was placed over the silver eight turn antenna coil. The silver capacitive plate was placed face down on the PE and aligned with the silver image below. The sample was then hot pressed with a 220°C iron. The two PEN film substrates were then carefully peeled away leaving the silver films transferred in tact on either side of the PE substrate. After transfer, the electrical resistivity properties remained the same.

#### **Example 2**

The procedure of Example 1 was repeated except that only the capacitive plate was screen printed and thermally cured using the silver screen ink prepared in Example 1. The eight turn antenna coil was etched aluminum on a 1 mil thick PE substrate. The silver capacitive plate was transfer laminated to the aluminum coil as was done in Example 3 with similar results.

#### **Example 3**

The procedure of Example 2 was repeated except that the capacitive plate was printed and thermally cured on a DuPont Kapton® H polyimide film. Similar results were obtained with the transfer lamination.

#### **Example 4**

The procedure of Example 2 was repeated except that the capacitive plate was printed and thermally cured on a DuPont Kapton® FN FEP Teflon coated polyimide film. Similar results were obtained with the transfer lamination.



### Example 5

Copper PARMOD™ ink was prepared by mixing 47 grams of copper flake, 29 grams of nanometer sized spherical copper powder mixed with neodecanoic acid (~77 wt% metal) and 15 grams of neodecanoic acid in a glove box. This premix was then further mixed on a 2-roll mill for 30 minutes in air. The gap setting on the mill was 0.006" - 0.008". After milling, the ink was removed from the mill and stored in a plastic syringe from which is also was dispensed.

The copper PARMOD™ ink was screened onto aluminum foil and fired at 360°C for 3 minutes in a N<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub> gas mix. The resulting copper circuit produced did not adhere well to the aluminum foil substrate. The resulting circuit was peeled off the substrate using 2 inch wide pressure sensitive, adhesive coated cellophane tape which was then stuck to a paper backing.

### Example 6

Copper PARMOD™ ink was prepared by mixing 49 grams of copper flake, 31 grams of nanometer sized spherical copper powder mixed with neodecanoic acid (~77 wt% metal) and 11 grams of neodecanoic acid in a glove box. This premix was then further mixed on a 2-roll mill for 30 minutes in air. The gap setting on the mill was 0.006" - 0.008". After milling, the ink was removed from the mill and stored in a plastic syringe from which is also was dispensed.

An aqueous suspension of boron nitride powder was sprayed onto an alumina substrate (0.030" thick) and allowed to dry in air. Excess boron nitride was removed by wiping with a lint free cloth.

The copper PARMOD™ ink was screened onto the boron nitride coated alumina substrate in the form of an antenna coil for a radio frequency tag and fired at 360°C for 3 minutes in a N<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub> gas mix. The resulting antenna coil did not adhere well to the alumina substrate and it was transferred to a 0.004 " polyester sheet coated with pressure sensitive adhesive. The same process was repeated for the

capacitor portion of the tag, and the antenna coil and the capacitor were then "laminated" together using rubber cement deposited on both sides of Kapton, which serves as the dielectric.

#### **Example 7**

Copper PARMOD™ ink was prepared by mixing 48 grams of 9 micron diameter spherical copper powder, 30 grams of 3 micron diameter spherical copper powder, 15 grams of nanometer sized spherical copper powder mixed with neodecanoic acid (~77 wt% metal) and 7 grams of neodecanoic acid in a glove box. This premix was then further mixed on a 2-roll mill for 30 minutes in air. The gap setting on the mill was 0.006" - 0.008". After milling, the ink was removed from the mill and stored in a plastic syringe from which it was also dispensed.

The copper PARMOD™ ink was screened onto unclad Teflon-glass laminate (0.062" thick) and fired at 300°C for 6 minutes in a N<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub> gas mix. The resulting copper circuit produced did not adhere well to the Teflon-glass laminate case of the epoxy-glass.

The copper circuit on the Teflon-glass rigid board was transferred to a rigid FR-4 glass-epoxy substrate by lamination using an acrylic sheet adhesive (DuPont LF0120). An epoxy prepreg was used to adhere the Kapton to the FR-4 board. The lamination conditions were ~350 Psi laminating pressure and a vacuum of 28 in Hg for 60 minutes at 190°C. The resulting bright copper circuit was well adhered to the Kapton. After submersion in a 255°C solder bath for 20 seconds, there were no signs of delamination, and the solder adhered well to the copper, which had been immersed in flux prior to being introduced into the solder bath.

**Example 8**

Copper PARMOD™ ink was prepared by mixing 48 grams of 9 micron diameter spherical copper powder, 30 grams of 3 micron diameter spherical copper powder, 15 grams of nanometer sized spherical copper powder mixed with neodecanoic acid (~ 77 wt% metal) and 7 grams of neodecanoic acid in a glove box. This premix was then further mixed on a 2-roll mill for 30 minutes in air. The gap setting on the mill was 0.006" – 0.008". After milling, the ink was removed from the mill and stored in a plastic syringe from which it also was dispensed.

Copper PARMOD™ ink was screened onto unclad Teflon-glass laminate (0.062" thick) and fired at 300°C for 6 minutes in a N<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub> gas mix. The resulting copper circuit produced did not adhere well to the Teflon-glass laminate.

The copper circuit on the Teflon-glass rigid board was transferred to a rigid, glass-polyester substrate by lamination using an acrylic sheet adhesive (DuPont LF0120). The lamination conditions were ~350 Psi lamination pressure and vacuum pressure of 28 in Hg for 60 minutes at 190°C. The resulting bright copper circuit was well adhered to the acrylic. After submersion in a 255°C solder bath for 20 seconds, there were no signs of delamination, and the solder adhered well to the copper, which had been immersed in flux prior to being introduced into the solder bath.

While the invention has been described with reference to preferred embodiments thereof, it will be appreciated by those of ordinary skill in the art that modifications can be made to the structure and form of the invention without departing from the spirit and scope thereof.

### What is Claimed

**Claim 1.** A method for producing one or more patterned metal objects on a substrate comprising the steps of :

a) applying a metal composition which can be thermally cured at low temperatures and in short times to form pure metal conductors on a thermally resistant temporary substrate in the patterns of the one or more patterned metal objects;

b) curing said metal composition with heat to form the one or more patterned metal objects;

c) transferring the one or more patterned metal objects from said temporary substrate to one side of the substrate.

**Claim 2.** The method of claim 1 further comprising the steps of:

d) applying a metal composition which can be thermally cured at low temperatures to form pure metal conductors on a second thermally resistant substrate in the patterns of additional one or more patterned metal objects;

e) curing said metal composition with heat to form said additional one or more patterned metal objects;

f) transferring said additional one or more patterned metal objects from said second temporary substrate to the side of the substrate opposite the side to which said one or more patterned metal objects were transferred in step c).

**Claim 3.** The method of claim 1 wherein said metal composition is applied to said temporary substrate using a method selected from the group consisting of screen printing, stenciling, dispensing, gravure printing, ink jet printing, impression printing, offset printing and electrostatic printing.

**Claim 4.** The method of claim 1 wherein said temporary substrate is in the form of a continuous belt.

**Claim 5.** The method of claim 1 wherein said one or more patterned metal objects comprises Tape Automated Bonding Decals.

**Claim 6.** The method of claim 1 wherein said one or more patterned metal objects comprises strain gauges.

**Claim 7.** The method of claim 1 wherein said one or more patterned metal objects comprises thermocouples.

Claim 8. The method of claim 1 wherein said temporary substrate is selected from the group consisting of polyimide films, polysulfone films, polyester films, teflon coated films, silicone coated films, metal foils, glass and ceramic surfaces.

Claim 9. The method of claim 1 wherein substrate is selected from the group consisting of polyethylene, polypropylene, polystyrene, polyester, polycarbonate, polyurethane, cellulose and paper.

Claim 10. The method of claim 1 wherein the substrate is in the form of a tape or continuous web.

Claim 11. The method of claim 1 wherein said metal composition is comprised of metal particles and a reactive organic medium, wherein said reactive organic medium is comprised of a decomposable compound or one or more reagents which form a decomposable compound with said metal particles

Claim 12. The method of claim 11 wherein said decomposable compound in the reactive organic medium has a weak hetero atom bond to the metal such that it will decompose at a temperature which said temporary substrate can withstand.

Claim 13. The method of Claim 12 wherein said hetero atom is selected from the group consisting of O, N, S, P, and As.

Claim 14. The method of Claim 11 in which said metal particles are selected from the group consisting of the group IB, IIB, IVA, VA, VI A, VII A and VIIIA metals, indium, tin, antimony, lead and bismuth.

Claim 15. The method of claim 2, wherein step f) comprises placing a double sided dielectric over said one or more patterned objects and then transferring said additional one or more patterned metal objects from said second temporary substrate to said double sided dielectric.

FIGURE 1

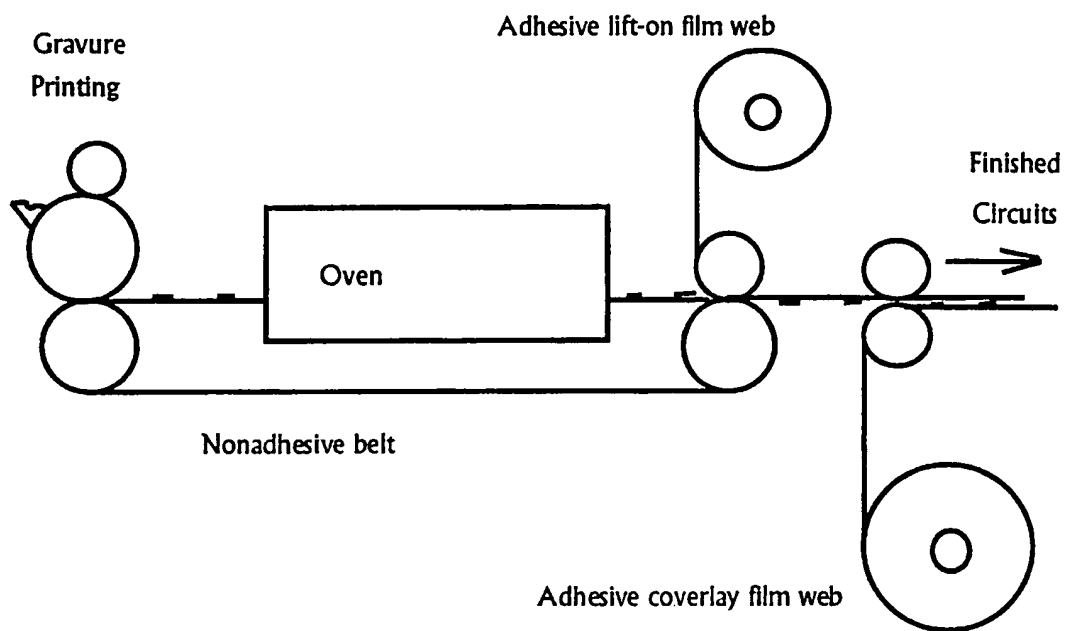


FIGURE 2

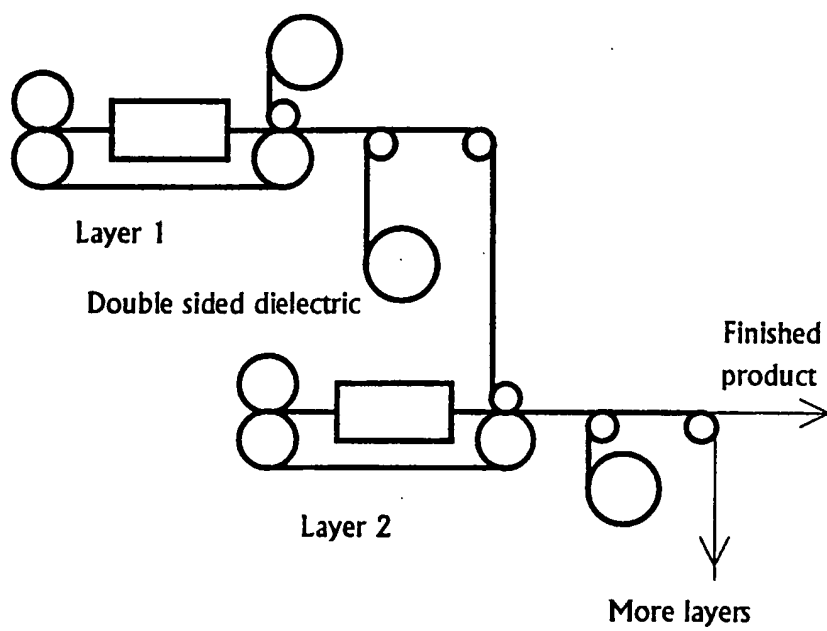
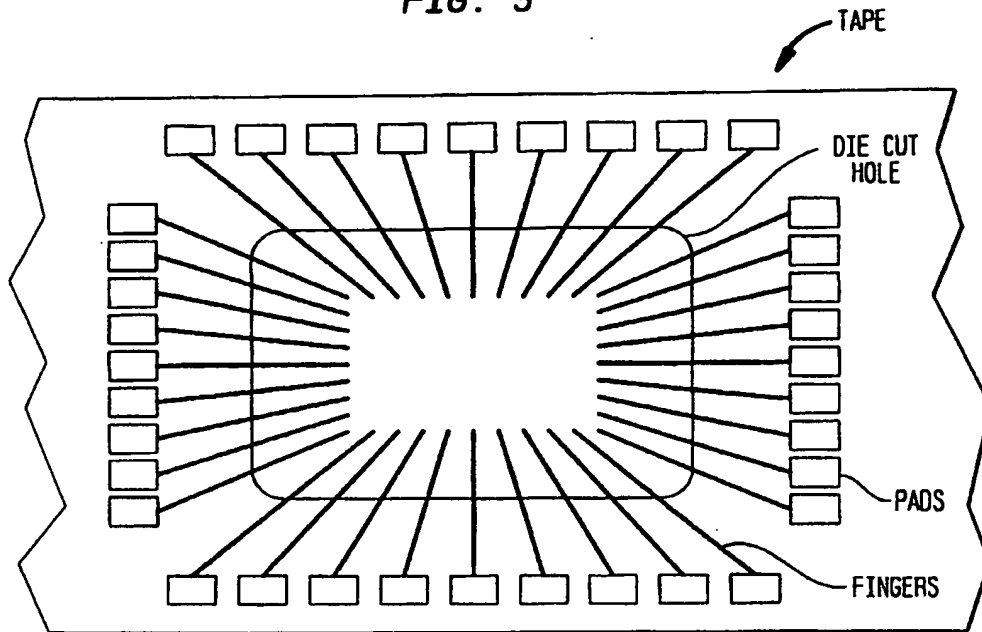


FIG. 3





## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/20420

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B29B 31/00; B32B 31/00; B44C 1/165

US CL :156/230, 231, 233, 238, 240, 241, 247, 277, 289

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 156/230, 231, 233, 238, 240, 241, 247, 277, 289

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS search terms: circuit?, pattern?, carrier?, transfer?, print?, metal?, neodecanoate?, silver, gold, copper, hexanoate?

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,775,439 A (SEEGER, JR., et al) 04 October 1988 (04.10.88), see entire document especially abstract, column 1, lines 35-53, column 2, lines 22-26, column 3, lines 1-62.	1-3
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Y		4-10
Y	US 5,059,242 A (FIRMSTONE et al) 22 October 1991 (22.10.91), see entire document especially abstract, column 2, lines 51-68, column 5, lines 36-37, column 7, lines 49-68, column 8, lines 1-23, column 10, lines 14-51.	11-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

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12 DECEMBER 1998

Date of mailing of the international search report

29 JAN 1999

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